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**PATENT ABSTRACTS OF JAPAN, vol. 10, no.**  
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**PATENT ABSTRACTS OF JAPAN, vol. 10, no.**

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**JP-A-61 167 567 (FUTJITSU Ltd.) 29-07-1986**

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**EP 0 367 438 B1**

## Description

The invention relates to a method of reducing the wettability of the surface of a substrate by providing an adherent layer of fluorosilane on the surface, and to an ink jet recording head including a surface coated with such a layer.

The ink jet recording method is a method wherein recording liquid (i.e. ink) is jetted in the form of droplets from an ink jet recording head toward a receiving surface such as of paper on which the droplets are deposited to effect printing.

In one such method, generally referred to as the continuous method, a stream of electrically charged ink droplets is generated while controlling the charge by a continuous oscillation generating means. The droplets, each with a controlled level of electric charge, are jetted towards the receiving surface, e.g. a paper sheet, and the flying course of the droplets is controlled by a pair of deflecting electrodes to which an electric field is applied and between which the droplets pass.

In another such method, generally referred to as the drop-on-demand method, a piezoelectric oscillator is mounted on the ink jet recording head and is mechanically oscillated by application of an electric recording signal.

Typically, the recording head includes a fine pipe for the ink which opens into an orifice. The surface surrounding the orifice may be of the same material as the pipe, or the orifice may be formed in a plate, called the orifice plate, which is attached to the end of the pipe and may be of a material different from that of the pipe. For the purposes of this invention, the orifice plate, if present, is considered to form part of the recording head.

In either case, it has been found desirable for at least a part of the surface of the head to have poor wettability toward the solvent employed for the ink. In some cases, it is also desirable for another part of the surface to have good solvent-wettability. For example, in some head designs, it has been found desirable for at least one part of the surface to remain essentially unwetted by the ink, in order to avoid problems of reliability in operation, and for at least another part to be wettable, e.g. so that another component may be bonded to the face of the head. In one specific embodiment it has been found that where the surface of the area surrounding the orifice is made from certain preferred non-vitreous materials such as metals, ceramics or plastics, problems can arise as a result of the ink wetting the surface and forming a pool which surrounds the orifice. This pool can interfere with the proper operation of the printer and prevent continuous operation of the printer for more than short periods of time.

There is therefore a need for at least a part of the surface of the recording head, e.g. that part surrounding the orifice, to be treated so that it is less readily wettable by liquids, and in particular by the ink or, more particularly, by the solvent employed in the formulation of the ink, and much research time has been expended on resolving this need; see, for example, U.S. Patent Nos. 4,555,062, 4,623,906 and 4,343,013, and European Patent Publication Nos 0177316A, 0092229A, 0092230A and 0121623A.

It is known that the tendency of a surface to be wetted by water or other solvents of the kind used in ink formulations can be reduced by coating the surface with an organic fluoro compound. However, it has been found that prior proposals for applying such fluoro compounds to the surfaces of non-vitreous substrates such as of metal, ceramics or plastics suffer from one or more disadvantages. For example, PTFE does not have the desired non-wettability for some of the preferred solvents and is difficult to bond to some surfaces. Coatings of fluorinated polymers of the kind proposed for use in microcircuitry, on the other hand, do not adhere sufficiently strongly and could be removed during normal procedures used for cleaning the head, such as wiping. Examples of such coatings are SC-721 marketed by 3M, Nyebar marketed by Nye, and Galydene marketed by Montedison.

U.S. Patent No. 4,643,948 proposes coating the surface of an ink jet recording head with a partly fluorinated alkyl silane and a perfluorinated alkane; however, the only method described for forming the coating involves radio frequency glow discharge.

IBM Technical Disclosure Bulletins Vol. 23, No. 1 of June 1980; Vol. 26, No. 1 of June 1983; and Vol. 26, No. 3A of August 1983; and U.S. Patent No. 4,368,476 are representative of proposals for treating the recording head face with a fluorosilicon compound, e.g. by dipping the surface in a dilute solution of the compound. However, it has been found that while some of the coatings could exhibit adequate non-wetting characteristics, their adhesion to non-vitreous surfaces, especially plastics surfaces, is inadequate.

The chosen surface layer, of course, must also be resistant to the ink solvent and this has presented a particular problem in the case of some of the solvents which are now gaining favour, such as those of the glycol or glycol ether kind. For example, it is known, for example from Japanese Kokai 74-31767, to vacuum coat a plastics surface with silicon oxide film and then apply a coating of fluorosilane; however, it has been found that the surface of the coated product thereby obtained is crazed by contact with some of the preferred ink solvents. The layer, e.g. coating, which provides

the desired non-wetting characteristics must also adhere well to the substrate, be abrasion resistant, and be resistant to attack by solvents employed in inks used in ink jet printing. Adhesion presents a particular problem where the substrate is non-vitreous and especially where it is formed of plastics material.

U.S. Patent No. 3,953,115 describes forming an adherent optically clear abrasion resistant coating on a plastic ophthalmic substrate, using a partially hydrolysed solution of a vinyl tri(lower alkoxy) silane. U.S. Patent No. 4,006,271 applies a solution of a hydrolysed C<sub>1-2</sub> alkyl tri(lower alkoxy) silane to a polycarbonate.

The present invention provides a method of providing a coating which exhibits good non-wetting characteristics toward a variety of solvents such as in particular those employed in inks and yet which is bonded well to a plastics or other non-vitreous inorganic material such as may be employed to provide the surface surrounding the jet orifice of an ink jet recording head, and exhibits good abrasion resistance and resistance to solvent attack.

According to the present invention there is provided an ink jet recording head of the kind in which ink droplets are jetted from a jet orifice of the head towards a recording material and wherein the surface of at least the area of the head surrounding the jet orifice comprises plastics or non-vitreous inorganic material and said surface is coated with a fluorosilane layer which reduces the wettability of the surface, wherein a first layer comprising cured siloxane which is adherent to said surface is interposed between said surface and said fluorosilane layer and said fluorosilane layer is derived from at least one fluorosilane having at least one hydrolysable group attached to a silicon atom.

By a "fluorosilane" is meant a silicon compound having at least one fluorinated organic group attached to a silicon atom. The term "non-vitreous" denotes materials not made of glass.

There is also provided a method of reducing the wettability of a surface comprising plastics or non-vitreous inorganic material by providing an adherent layer of fluorosilane on said surface, said method comprising:

- (i) forming on said surface an adherent first layer comprising cured siloxane; and
- (ii) applying to said first layer a second layer comprising at least one fluorosilane having at least one hydrolysable group attached to a silicon atom and at least one fluorine-containing organic group attached to a silicon atom, said fluorine-containing organic group donating non-wetting properties to the second layer.

The present invention also provides an ink jet recording head of the kind in which ink droplets are jetted from a jet orifice of the head towards a recording material and wherein the surface of the head has at least one zone which exhibits good solvent-wettability and at least one zone which exhibits poor solvent-wettability and said latter zone comprises a layer of fluorosilane bonded to the surface by means of an intermediate layer comprising cured siloxane.

While the invention may be applied to a variety of non-vitreous inorganic surfaces such as those of metal or ceramics, it finds special benefit in its application to surfaces of plastics material. Examples of such surfaces are those of acrylics, polyimide, polycarbonate, polyester, polyether ether ketone, and polyolefin, e.g. polyethylene; however, the invention is particularly important for the treatment of laser-ablatable plastics materials because the first and second layers can also be rendered laser-ablatable, thereby enabling the formation of orifices in an ink jet recording head after the wettability of the surface of the head has been reduced in accordance with the invention, and thus reducing the number of steps required to form the orifices.

The plastics material whose surface may be treated by the process of the present invention may include additives of the kind normally employed with plastics, including organic and/or inorganic fillers; however, the surface itself is preferably essentially, i.e. substantially entirely, plastics material.

The adherent cured siloxane layer is obtainable by coating the surface with a silane and treating the coating to interlink the silane molecules of the coating, i.e. polymerise the silane, by the development of Si-O-Si linkages and thereby effect curing. In general, this is achieved by choosing as the silane a compound having hydrolysable groups and a non-hydrolysable organic group attached to a silicon atom and hydrolysing at least some of the hydrolysable groups to form Si-OH groups which are then caused to react with corresponding groups, or with hydrolysable groups e.g. alkoxy groups attached to Si atoms of other molecules in the layer, to form Si-O-Si linkages with loss of water or other by-product of the condensation.

Normally, the silane will be applied in the form of a solution, the solvent of which is then removed, e.g. by volatilisation.

To achieve the desired adherent cured siloxane layer, it is preferred that all but one of the radicals attached to a silicon atom be hydrolysable groups. Preferably, the hydrolysable groups are selected from alkoxy groups since the hydrolysis products are alcohols which, with appropriate choice of the solvent, can readily be removed with the solvent.

Most preferably, the alkoxy group has up to 3 carbon atoms.

The nature of the other group attached to the silicon atom of the silane chosen to form the siloxane layer will depend at least in part upon the nature of the surface to be coated. The bond between the first layer and the surface may be chemical, e.g. by reaction of active groups in the silane with groups reactive therewith in the surface to be coated, or it may be physicochemical e.g. as in Van de Waal's bonds (that is, dipole-dipole bonding), hydrogen bonding or  $\pi$  -  $\pi$  bonding. For example, where the substrate is a polymer containing residues of a benzene or other aromatic or pseudoaromatic ring, e.g. as in aromatic polyimides, aromatic polyether-ether-ketones and aromatic polycarbonates, and adhesion to the substrate is achievable by  $\pi$  -  $\pi$  bonding, the silane may contain at least one group having  $\alpha,\beta$ -ethylenic unsaturation, e.g. an allyl group. Alternatively, where, for example, the substrate surface contains OH groups and adequate adhesion by hydrogen-bonding is achievable, the silane may desirably contain at least one group containing an active or Zerewitinoff hydrogen atom, e.g. as in a primary or secondary aminoalkyl.

Preferably, therefore, in accordance with one embodiment of the invention the silane satisfies the formula



where each R is an alkyl group and Y is a non-hydrolysable monovalent organic radical. Suitably, Y is a saturated or unsaturated monovalent hydrocarbon group or a substituted derivative thereof. For reasons such as availability or ease of synthesis of the compounds and cost, Y will generally be selected from alkyl and alkenyl groups especially those containing 1 to 6 carbon atoms, and substituted derivatives thereof wherein each substituent is selected from halogen, alkoxy and primary, secondary or tertiary amino. Examples of such groups are methyl, ethyl, allyl, methallyl,  $\gamma$ -aminopropyl,  $\gamma$ -methylaminopropyl,  $\gamma$ -dimethylaminopropyl, and methoxyethyl.

A particularly good combination of adhesion to the substrate surface and resistance to abrasion is obtained if the silane employed to form the adherent cured siloxane coating comprises a mixture of silanes which includes a silane containing a primary, secondary or tertiary aminoalkyl group; preferably a mixture of at least one first silane selected from primary, secondary and tertiary-aminoalkyl trialkoxysilanes and at least one second silane selected from alkyl trialkoxysilanes, preferably where the alkyl and alkoxy groups each contain up to 3 carbon atoms. Particular good results are

achieved from a mixture of a major amount of alkyl trialkoxy silane and a minor amount of aminoalkyl trialkoxysilane, e.g. from 75 to 60% by weight of the former and from 25 to 40% by weight of the latter. Examples of suitable compounds are methyl triethoxysilane and  $\gamma$ -aminopropyl triethoxysilane.

However, where laser ablatability of the siloxane layer is important, it may be desirable to include in the cured siloxane layer a photoabsorbing molecule to assist the ablation or to form the siloxane layer from a silane having good photoabsorption characteristics, or from a mixture of silanes which includes a silane having such characteristics. Examples of silanes having the desired characteristics are those which include aliphatic carbon-carbon unsaturation, e.g. as in an allyl group or a methallyl group. Thus, in this embodiment of the invention some or all of the alkyl trialkoxysilane may be replaced by alkenyl trialkoxysilane, e.g. allyl triethoxysilane.

Preferably, the silane or silane mixture employed to form the siloxane layer is at least partially hydrolysed prior to its application to the substrate so as to facilitate subsequent curing of the layer. This may be achieved, for example, by standing a solution of the silane over water. Hydrolysis may be assisted by dilute acid.

Where the silane or mixture of silanes is applied as a solution, any suitable solvent or solvent mixture may be employed. Preferably, a solvent having a low boiling point is employed so that it is readily removable by evaporation. However, too high a rate of solvent removal may generate stresses in the layer which could lead to crazing. It may therefore be desirable to include a small proportion of a tail solvent.

One method of achieving the preferred cured siloxane layer thickness of not more than a few microns, e.g. 0.01 to 10 microns, is to apply a solution of the silane by spin-coating. Removal of the solvent and curing may be achieved by heat. It is preferred that the cured layer contains some free hydroxyl groups attached to silicon atoms, i.e. Si-OH groups, since this appears to assist the bonding of the second layer. This may be achieved, for example, by effecting at least the final stages of the heating step in the presence of water vapour. However, this is not essential.

Thus, one preferred method of forming the cured siloxane layer comprises spin-coating the surface with a solution of the silane wherein the silane is in an at least partially hydrolysed form, and thereafter heating the coated surface to drive off the solvent and cure the silane until an adherent coating is obtained.

In addition to enabling the adhesion of the fluorosilane layer to the substrate, the presence of the cured siloxane layer may also provide other

benefits. One is that it assists planarisation of the surface thereby enhancing the non-wetting characteristics of the surface of the eventual fluorosilane-coated product. Another is that in the case of the preferred plastics surfaces such as polyimide it improves the durability and scratch resistance of the product and hence its ability to withstand mechanical handling.

In the second step of the process, a layer derived from at least one fluorosilane is applied to the cured siloxane layer. The fluorosilanes suitable for use in this step are chosen from those having at least one hydrolysable group attached to a silicon atom and at least one fluorine-containing organic group attached to a silicon atom, the fluorine-containing organic group being one which donates desired non-wetting properties to the layer.

In one embodiment, the fluorosilanes may be selected from those satisfying the formula:



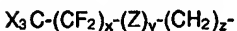
where m and n are integers, m is one or two, n is at least two, and the sum of m plus n is four, each  $R^2$  is a fluorine-containing organic group and each  $R^3$  is a hydrolysable group. Preferred hydrolysable groups are alkoxy, most preferably containing 1 to 3 carbon atoms.

While m may be 1 or 2, it is not thought that any improvement in anti-wetting properties is achieved where m is 2 and on the other hand the adhesion to the first layer may be reduced. Therefore, it is preferred that m is 1 and n is 3.

The anti-wetting properties donated by the fluorosilane layer tend to be a function of the nature of  $R^2$ . In general, the anti-wetting properties improve with increase in the degree of fluorination of the terminal region of  $R^2$ ; that is, the region of  $R^2$  at or towards the other end of  $R^2$  from that by which it is attached to the Si atom. Preferably  $R^2$  will contain at least one  $CF_3$ - group in the terminal region.

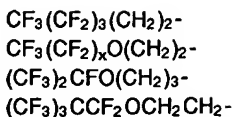
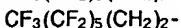
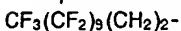
The group to which the fluorine atoms are attached may be any suitable organic group, but generally it will be a saturated group, e.g. alkyl, alkoxyalkyl or alkylcarboxyalkyl.

For example,  $R^2$  may have the structure



where each x is F or  $CF_3$ , Z is a divalent atom or group such as -O-, each of x and z is zero or a positive integer and y is zero or one. One or more of the fluorine atoms in each - $CF_2$ - group may also be replaced by a - $CF_3$  group, if desired.

Specific examples are:



One or more of the  $R^2$  and/or  $R^3$  groups may be replaced by another monovalent atom or group, it being understood, of course, that the molecule retains at least one fluorine-containing group and at least one hydrolysable group and that said other group does not prevent hydrolysis or adversely affect the non-wetting properties of the layer to an undesirable extent.

In accordance with this modification, the fluorosilane may have the formula



where  $R^2$  and  $R^3$  are as defined above, each  $R^4$  is a non-hydrolysable atom or group other than  $R^2$ , is 1 or 2, n is at least 1, p is 0, 1 or 2 and  $m+n+p=4$ ; where  $R^4$  is said other monovalent atom or group. An example of such an atom or group is F.

The fluorosilane layer may be formed by vacuum deposition from vapour of the fluorosilane and it has been found desirable to keep the humidity low to obtain the best adhesion. Alternatively, it may be applied as a solution in a suitable solvent which is then removed, e.g. by evaporation.

It is believed that the adhesion of the fluorosilane layer to the siloxane layer involves reaction of the hydrolysable groups  $R^3$ . Where the first layer contains Si-OH groups it is believed that heating the second layer effects chemical reaction between hydrolysable groups  $R^3$  of the second layer and Si-OH groups of the first layer and achieves a chemical bond between the layers.

Whether or not actual chemical bonding occurs, it is in any event preferred to heat the second layer in contact with the first layer to achieve optimum adhesion.

Best results are obtained when the second layer is 5 microns thick or less. Above 5 microns little or no further improvement in anti-wetting properties is obtained and on the other hand, good results are achievable even with a layer which is only a few molecules, e.g. one or two molecules, thick.

Ink solvents with which the ink jet recording heads according to the present invention may be successfully employed include alcohols (e.g. isopropyl alcohol), halogenated organics (e.g. 1,1,1 trichloroethane) aromatic hydrocarbons (e.g. xylene), ketones (e.g. acetone), water, and solvents of the type based on naphthenic and paraffinic hydrocarbons and their mixtures (e.g. the solvent sold as "Vista 47") as well as the more aggressive glycol and glycol ether solvents such as the monomethyl ethers of di- and tri-propylene glycol,

ethylene glycol butyl ether and diethylene glycol butyl ether.

The invention will now be illustrated with reference to an Example and with the aid of the accompanying drawings in which

Figure 1 is a schematic cross-sectional view of an ink jet recording head provided with a non-wetting coating according to the invention, Figure 2 is a schematic diagram of an apparatus for measuring receding angle, and

Figure 3 is a schematic diagram illustrating measurement of receding angle using the apparatus of Figure 2.

In Figure 1, a part of an ink jet recording head 2 of "Kapton" polyimide is provided with orifices 4 opening into ink conduits 6, and a non-wetting coating, generally designated 8, comprising an adherent first layer 10 of cured siloxane and a second layer 12 of fluorosilane.

The non-wetting coating 8 was made in two stages, designated A and B. In the first stage (A), a thin cured siloxane layer having residual free -OH groups was formed from solution on the surface of the Kapton polyimide. In the second stage (B) a fluorosilane was chemically coupled to the siloxane layer 10 to form a non-wetting surface. In the following description, all parts are by volume except where otherwise indicated.

#### (A) Formation of Siloxane Coating

13.75 parts methyl triethoxysilane (MTES) were mixed with 12.5 parts 0.01N HCl and 12.5 parts absolute ethanol in a clean glass vessel and allowed to stand for at least 3 hours to allow partial hydrolysis of the MTES to occur.

The coating solution was then made from 15 parts of the resultant solution, 0.25 part of acetic acid, 2 parts of ethylene glycol monohexyl ether and 2.5 parts of aminopropyl triethoxysilane and immediately filtered through a 2 micron filter. The filtered product had a working lifetime of 30 minutes to 1 hour.

Samples of Kapton polyimide sheet were cleaned using isopropanol and then coated with the solution by spin-coating to give a film of between 0.5 and 2 microns thick. The coating was allowed to air dry before being baked at 50°C for 30 minutes, followed by 30 minutes at 45°C and 95% relative humidity.

#### (B) Application of Fluorosilane Layer

300 parts of 1H,1H,2H,2H perfluorooctyl triethoxysilane (PFOTES) in a large shallow metal dish lined with aluminium foil were placed in the bottom of a dessicator and siloxane-coated Kapton polyimide sheets from stage (A) were arranged in a

rack in the upper section of the chamber so that the siloxane coated surface of each was freely exposed.

The chamber was evacuated to approximately 50 torr for 10 minutes, brought up to room pressure using dry nitrogen, then re-evacuated to 50 torr for a further 10 minutes to reduce the relative humidity to less than 10%.

The dessicator was then sealed, disconnected from the vacuum pump, placed for 2 hours in an oven which had been preheated to 180°C, and then allowed to cool for 15 minutes before being reconnected to the vacuum pump. The dessicator was then evacuated while it continued to cool. The samples were then removed after bringing the chamber back up to room pressure using dry nitrogen gas.

The samples were then submitted to a number of tests, described below, to assess their suitability for use in the production of ink jet recording heads.

The non-wetting characteristics in relation to ink solvents were assessed from the receding contact angle as measured by the following test procedure and using the apparatus diagrammatically illustrated in Figures 2 and 3 comprising a metal sample holder 20 of which the dimensions AB and BC were each 30 mm, a polypropylene tube 22 having an open end 24 and a free end 26, a travelling microscope 28 and a sample 30 having a coated surface 32 to be tested and a piece of double-sided adhesive tape 34. An eye-piece 36 of the travelling microscope 28 has a cross hair graticule one arm 38 of which is aligned with a mark on the external casing of the eye-piece (Figure 3). A scale 40 is marked around the cylindrical body of the eye-piece 36.

The polypropylene tube 22 is partially filled with the chosen solvent and placed in the metal holder 20 such that the open end 24 is firmly suspended about 2 mm above the coated surface 32 of the sample 30. The free end 26 is placed in a clamp so that it can be moved up and down. The intervening length of tube 22 is constrained into an S-shape, as shown. By moving the free end 26 of the tube 22 up and down slowly it is possible to expel a drop of liquid 42 onto the surface 32 and suck it back up.

The liquid drop is illuminated at grazing incidence using a diffused light source (not shown). The drop and its reflected image are viewed through the travelling microscope 28. By rotating the eye-piece relative to the main body and noting the position of the external mark on the eye-piece, an angular measurement of the position of the arm 38 of the cross-hair can be made.

A freshly prepared sample 30 is positioned on the base of the sample holder using the double sided tape 34 and the liquid in the tube 22 is

induced to flow over the surface 32 for a distance of a few millimetres by slowly raising the free end 26 of tube 22. After waiting for the liquid position to stabilise and become stationary, the free end 26 of the tube 22 is slowly lowered, thereby causing the liquid to be sucked back up the tube and the drop to be retracted back across the surface. When the drop has stabilised and become stationary in the retracted position, the receding angle is measured as the angle between the surface of the drop 42 (Figure 3) and the sample surface at the point of contact of the drop with the surface. Both the angle of the actual drop 42 and that of its reflected image 44 are measured. With the microscope aligned so that the crossing point of the cross hairs is on the point of contact between the drop and the sample surface, measurement is effected by rotating the eye-piece so that the marked arm 38 of the cross hair is aligned first with the surface of the drop (position y in Figure 3) and then with the image of that surface (position x in Figure 3). The receding angle  $\alpha = 90 + \beta/2$  where  $\beta$  is the angle between x and y.

In general, a receding angle  $\alpha$  of  $150^\circ$  or less is considered adequate.

Using tripropylene glycol monomethyl ether (TPM) as the liquid, a receding contact angle of  $130^\circ$  was observed, illustrating excellent non-wetting properties of the surface of the coated samples.

Abrasion resistance was evaluated by stroking a cotton bud soaked in solvent (TPM) across the surface of the sample. The non-wetting properties of the surface were still apparent after 1,000 strokes. By way of example, where the Kapton polyimide samples were coated with proprietary coatings such as Nyabar and Galydene, the non-wetting properties were lost after 1 to 10 passes with the soaked cotton bud.

The coated Kapton polyimide samples could be bent back on themselves, i.e. through about  $180^\circ$ , without cracking, thus indicating excellent adhesion of the coating to the plastics.

Resistance to solvents was assessed by immersing the samples in the solvent concerned. No crazing or other evidence of solvent attack was observed after at least fourteen days' immersion in each of the following solvents: acetone, water, diethylene glycol, tripropylene glycol monomethyl ether, paraffin, and Vista '47.

Similar results to those described above were also obtained using 1H, 1H, 2H, 2H-perfluorododecyl triethoxysilane as the fluorosilane.

By way of comparison, samples of Kapton polyimide coated with proprietary non-wetting coatings such as Nyabar and Galydene showed evidence of solvent attack in as little as a few hours when the same solvents were employed.

Ink jet recording head orifice plates were obtained from the coated sheets by cutting them to the desired size and then forming passages for the ink in them by laser ablation.

If it is desired for part or parts of the surface of the orifice plate to be wettable, the sheets may be masked appropriately prior to coating.

"Vista", "Kapton", "Nyabar" and "Galydene" are trade names which may be registered as Trade Marks in one or more of the territories designated by this application.

## Claims

1. A method of reducing the wettability of a surface comprising plastics or non-vitreous inorganic material by providing an adherent coating of fluorosilane on said surface, said method comprising:
  - (i) forming on said surface an adherent first layer comprising cured siloxane; and
  - (ii) applying to said first layer a second layer derived from at least one fluorosilane having a silicon atom to which is attached at least one hydrolysable group and at least one fluorine-containing organic group which donates non-wetting properties to the layer.
2. A method as claimed in claim 1 in which said surface comprises an area surrounding a jet orifice of an ink jet recording head, the orifice being formed before or after the formation of the coating.
3. A method as claimed in claim 1 or claim 2 in which said layer of cured siloxane contains free hydroxyl groups attached to silicon atoms and said second layer is chemically bonded to said first layer by reaction with said hydroxyl groups.
4. A method as claimed in any one of claims 1 to 3 in which said fluorosilane layer is heated in contact with the siloxane layer.
5. A method as claimed in any one of claims 1 to 4 in which step (i) comprises coating said surface with at least one silane having hydrolysable groups and a non-hydrolysable organic group attached to a silicon atom and treating the resultant coating to develop a cured siloxane layer which is adherent to the surface.
6. A method as claimed in claim 5 in which said at least one silane is at least partially hydrolysed prior to its application to the surface.

7. A method as claimed in claim 5 or claim 6 in which the silane satisfies the formula



where each R is an alkyl group and Y is a monovalent non-hydrolysable organic radical.

8. An ink jet recording head of the kind in which ink droplets are jetted from a jet orifice of the head towards a recording material and wherein the surface of the head has at least one zone which exhibits good solvent-wettability and at least one zone which exhibits poor solvent-wettability and said latter zone comprises a layer of fluorosilane bonded to the surface by means of an intermediate layer comprising cured siloxane.

9. An ink jet recording head of the kind in which ink droplets are jetted from a jet orifice of the head towards a recording material, the surface of at least the area of the head surrounding the jet orifice comprising plastics or non-vitreous inorganic material and said surface being coated with a fluorosilane layer which reduces the wettability of the surface, wherein a first layer comprising cured siloxane which is adherent to said surface is interposed between said surface and said fluorosilane layer and said fluorosilane layer is derived from at least one fluorosilane having at least one hydrolysable group attached to a silicon atom.

10. An ink jet recording head as claimed in claim 9 in which said fluorosilane layer is chemically bonded to said cured siloxane layer by reaction with free hydroxyl groups attached to silicon atoms in said cured siloxane layer.

11. An ink jet recording head as claimed in claim 9 or claim 10 in which said cured siloxane is derived from at least one silane which satisfies the formula



where each R is an alkyl group and Y is a monovalent non-hydrolysable organic radical.

12. A method as claimed in claim 7 or ink jet recording head as claimed in claim 11 wherein said at least one silane comprises a mixture including a silane containing a primary, secondary or tertiary aminoalkyl group.

13. A method or ink jet recording head as claimed in claim 12 wherein said mixture comprises at

least one silane selected from alkyl trialkoxysilanes and alkenyl trialkoxy silanes and at least one silane selected from primary, secondary or tertiary aminoalkyl trialkoxysilanes.

14. A method or ink jet recording head as claimed in claim 13 in which the said mixture comprises methyl triethoxysilane and  $\gamma$ -aminopropylene triethoxysilane.

15. A method or ink jet recording head as claimed in any one of claims 1 to 14 in which the hydrolysable fluorosilane has the formula:



where m is 1 or 2, n is at least 1, p is 0, 1 or 2, the sum of m + n + p is 4, each R<sup>2</sup> is a fluorine-containing organic group, each R<sup>3</sup> is a hydrolysable group and each R<sup>4</sup> is a non-hydrolysable atom or group other than R<sup>2</sup>.

16. A method or ink jet recording head as claimed in claim 15 wherein m is 1, n is 3 and p is 0.

17. A method or ink jet recording head as claimed in claim 15 or claim 16 wherein each R<sup>3</sup> is an alkoxy group.

18. A method or ink jet recording head as claimed in claim 15, claim 16 or claim 17 in which the fluorosilane is selected from 1H, 1H, 2H 2H-perfluorooctyl triethoxysilane and 1H, 1H, 2H, 2H perfluorododecyl triethoxysilane.

19. A method or ink jet recording head as claimed in any one of claims 1 to 18 in which said surface comprises a plastics material selected from polyimide, polycarbonate, polyester and polyether-etherketone.

#### Patentansprüche

1. Verfahren zur Verringerung der Benetzbarkeit einer Oberfläche, die Kunststoffe oder nicht glasartiges anorganisches Material umfaßt durch Bereitstellung einer haftenden Fluorsilanbeschichtung auf dieser Oberfläche, bei dem man

(i) auf der Oberfläche eine haftende erste Schicht bildet, die gehärtetes Siloxan umfaßt, und

(ii) auf diese erste Schicht eine zweite Schicht aufbringt, die von mindestens einem Fluorsilan mit einem Siliciumatom, an dem mindestens eine hydrolysierbare Gruppe hängt, und mindestens einer fluorhaltigen organischen Gruppe, die der Schicht



unbenetzbare Eigenschaften verleiht, abgeleitet ist.

2. Verfahren nach Anspruch 1, bei dem die Oberfläche einen eine Strahldüse eines Tintenstrahl-  
aufzeichnungskopfes umgebenden Bereich  
umfaßt, die vor vor oder nach der Ausbildung  
der Beschichtung gebildet wird.

3. Verfahren nach Anspruch 1 oder 2, bei dem  
die Schicht aus gehärtetem Siloxan an Silici-  
umatome gebundene freie Hydroxylgruppen  
enthält und die zweite Schicht durch die Reak-  
tion mit diesen Hydroxylgruppen mit der ersten  
Schicht verbunden wird.

4. Verfahren nach einem der Ansprüche 1 bis 3,  
bei dem die Fluorsilanschicht in Kontakt mit  
der Siloxanschicht erhitzt wird.

5. Verfahren nach einem der Ansprüche 1 bis 4,  
bei dem man in Schritt (i) die Oberfläche mit  
mindestens einem Silan mit hydrolysierbaren  
Gruppen und einer an ein Siliciumatom gebun-  
denen nicht hydrolysierbaren organischen  
Gruppe beschichtet und die dabei entstehende  
Beschichtung behandelt, um eine gehärtete Si-  
loxanschicht zu entwickeln, die an der Oberflä-  
che haftet.

6. Verfahren nach Anspruch 5, bei dem minde-  
stens ein Silan vor dem Aufbringen auf die  
Oberfläche zumindest teilweise hydrolysiert  
wird.

7. Verfahren nach Anspruch 5 oder 6, bei dem  
das Silan die Formel



hat, in der R eine Alkylgruppe und Y einen  
einwertigen, nicht hydrolysierbaren organi-  
schen Rest bedeutet.

8. Tintenstrahlauzeichnungskopf von der Art, bei  
der Tintentröpfchen aus einer Strahldüse des  
Kopfes auf ein Aufzeichnungsmaterial gestrahlt  
werden, wobei die Oberfläche des Kopfes min-  
destens eine Zone umfaßt, die gute Lösungs-  
mittelbenetzbarkeit aufweist, und mindestens  
eine Zone, die schlechte Lösungsmittelbenetz-  
barkeit aufweist und eine Schicht aus Fluorsi-  
lan enthält, die durch eine gehärtetes Siloxan  
umfassende Zwischenschicht mit der Oberflä-  
che verbunden ist.

9. Tintenstrahlauzeichnungskopf von der Art, bei  
der Tintentröpfchen aus einer Strahldüse auf

ein Aufzeichnungsmaterial gestrahlt werden,  
wobei die Oberfläche mindestens des Kopfbe-  
reiches, der die Strahldüse umgibt, Kunststoffe  
oder nicht glasartiges anorganisches Material  
umfaßt und mit einer Fluorsilanschicht be-  
schichtet ist, die die Benetzbarkeit der Oberflä-  
che vermindert, in der eine erste, gehärtetes,  
an der Oberfläche haftendes Siloxan umfas-  
sende Schicht zwischen die Oberfläche und  
die Fluorsilanschicht, die aus mindestens ei-  
nem Fluorsilan mit mindestens einer an ein  
Siliciumatom gebundenen hydrolysierbaren  
Gruppe abgeleitet ist, gelegt wird.

10. Tintenstrahlauzeichnungskopf nach Anspruch  
9, bei dem die Fluorsilanschicht durch die Re-  
aktion mit freien, an die Siliciumatome gebun-  
denen Hydroxylgruppen in der Siloxanschicht  
chemisch mit der gehärteten Siloxanschicht  
verbunden werden.

11. Tintenstrahlauzeichnungskopf nach Anspruch  
9 oder 10, bei dem die gehärtete Siloxan-  
schicht aus mindestens einem Silan der For-  
mel



abgeleitet ist, in der R eine Alkylgruppe und Y  
einen einwertigen nicht hydrolysierbaren orga-  
nischen Rest bedeutet.

12. Verfahren nach Anspruch 7 oder Tintenstrah-  
aufzeichnungskopf nach Anspruch 11, bei dem  
mindestens ein Silan eine Mischung umfaßt,  
die ein Silan mit einer primären, sekundären  
oder tertiären Aminoalkylgruppe enthält.

13. Verfahren oder Tintenstrahlauzeichnungskopf  
nach Anspruch 12, bei dem die Mischung min-  
destens ein aus Alkyltrialkoxysilanen und Al-  
kenyltrialkoxysilanen ausgewähltes Silan und  
mindestens ein aus primären, sekundären oder  
tertiären Aminoalkyltrialkoxysilanen ausgewähl-  
tes Silan enthält.

14. Verfahren oder Tintenstrahlauzeichnungskopf  
nach Anspruch 13, bei dem die Mischung Me-  
thyltriethoxysilan und  $\gamma$ -Aminopropyltriethox-  
ysilan umfaßt.

15. Verfahren oder Tintenstrahlauzeichnungskopf  
nach einem der Ansprüche 1 bis 14, bei dem  
das hydrolysierbare Fluorsilan die Formel



hat, in der m 1 oder 2, n mindestens 1 und p

0, 1 oder 2 bedeutet, die Summe von  $m + n + p$  4 ist, jedes  $R^2$  eine fluorhaltige organische Gruppe, jedes  $R^3$  eine hydrolysierbare Gruppe und jedes  $R^4$  ein nicht hydrolysierbares Atom oder eine Gruppe, die nicht  $R^2$  ist, bedeutet.

16. Verfahren oder Tintenstrahlauzeichnungskopf nach Anspruch 15, bei dem  $m$  1,  $n$  3 und  $p$  0 ist.

17. Verfahren oder Tintenstrahlauzeichnungskopf nach Anspruch 15 oder 16, bei dem  $R^3$  eine Alkoxygruppe ist.

18. Verfahren oder Tintenstrahlauzeichnungskopf nach Anspruch 15, 16 oder 17, bei dem das Fluorsilan aus 1H, 1H, 2H 2H-Perfluorooctyltriethoxysilan und 1H, 1H, 2H, 2H-Perfluorodecyltriethoxysilan ausgewählt ist.

19. Verfahren oder Tintenstrahlauzeichnungskopf nach einem der Ansprüche 1 bis 18, bei dem die Oberfläche ein aus Polyimid, Polycarbonat, Polyester und Polyetheretherketon ausgewähltes Kunststoffmaterial umfaßt.

#### Revendications

1. Procédé pour réduire la mouillabilité d'une surface comprenant une matière plastique ou un matériau inorganique non vitreux par fourniture d'un revêtement adhérent de fluorosilane sur cette surface, ce procédé comprenant :

(i) la formation sur cette surface d'une première couche adhérente comprenant un siloxane durci; et

(ii) l'application sur cette première couche d'une seconde couche provenant d'au moins un fluorosilane ayant un atome de silicium auquel sont attachés au moins un groupe hydrolysable et au moins un groupe organique contenant du fluor qui confère des propriétés non mouillantes à la couche.

2. Procédé suivant la revendication 1, dans lequel cette surface comprend une zone entourant un orifice de jet d'une tête d'enregistrement à jet d'encre, l'orifice étant formé avant ou après la formation du revêtement.

3. Procédé suivant les revendications 1 ou 2, dans lequel cette couche de siloxane durci contient des groupes hydroxy libres attachés aux atomes de silicium et cette seconde couche est liée chimiquement à cette première couche par réaction avec ces groupes hydroxy.

4. Procédé suivant l'une quelconque des revendications 1 à 3, dans lequel cette couche de fluorosilane est chauffée en contact avec la couche de siloxane.

5. Procédé suivant l'une quelconque des revendications 1 à 4, dans lequel l'étape (i) comprend le revêtement de cette surface avec au moins un silane ayant des groupes hydrolysables et un groupe organique non-hydrolysable fixés à un atome de silicium, et le traitement du revêtement résultant pour développer une couche de siloxane durci qui adhère à la surface.

6. Procédé suivant la revendication 5, dans lequel ce silane au moins présent est au moins partiellement hydrolysé avant son application sur la surface.

7. Procédé suivant les revendications 5 ou 6, dans lequel le silane satisfait à la formule :



dans laquelle chaque R est un groupe alkyle et Y est un radical organique monovalent non hydrolysable.

8. Tête d'enregistrement à jet d'encre du type dans lequel des gouttelettes d'encre sont projetées à partir d'un orifice de jet de la tête en direction d'un matériau d'enregistrement et dans laquelle la surface de la tête a au moins une zone qui présente une bonne mouillabilité pour le solvant et au moins une zone qui présente une médiocre mouillabilité pour le solvant, cette dernière zone comprenant une couche de fluorosilane liée à la surface au moyen d'une couche intermédiaire comprenant un siloxane durci.

9. Tête d'enregistrement à jet d'encre du type dans lequel des gouttelettes d'encre sont projetées à partir d'un orifice de jet de la tête en direction d'un matériau d'enregistrement, la surface d'au moins la zone de la tête entourant l'orifice du jet comprenant une matière plastique ou un matériau inorganique non vitreux et cette surface étant revêtue d'une couche de fluorosilane qui réduit la mouillabilité de la surface, dans laquelle une première couche comprenant un siloxane durci qui adhère à cette surface est interposée entre cette surface et cette couche de fluorosilane et cette couche de fluorosilane dérive d'au moins un fluorosilane ayant au moins un groupe hydrolysable attaché à un atome de silicium.

10. Tête d'enregistrement à jet d'encre suivant la revendication 9, dans laquelle cette couche de fluorosilane est liée chimiquement à cette couche de siloxane durci par réaction avec des groupes hydroxy libres attachés aux atomes de silicium dans cette couche de siloxane durci.
11. Tête d'enregistrement à jet d'encre suivant les revendications 9 ou 10, dans laquelle ce siloxane durci provient d'au moins un silane qui satisfait à la formule :
- $$\text{YSi(OR)}_3$$
- dans laquelle chaque R est un groupe alkyle et Y est un radical organique monovalent non-hydrolysable.
12. Procédé suivant la revendication 7 ou tête d'enregistrement à jet d'encre suivant la revendication 11, dans lequel ce silane au moins présent comprend un mélange comprenant un silane contenant un groupe aminoalkyle primaire, secondaire ou tertiaire.
13. Procédé ou tête d'enregistrement à jet d'encre suivant la revendication 12, dans lequel ce mélange comprend au moins un silane choisi parmi des alkyl trialkoxysilanes et des alcényl trialkoxy silanes et au moins un silane choisi parmi des aminoalkyl trialkoxysilanes primaires, secondaires ou tertiaires.
14. Procédé ou tête d'enregistrement à jet d'encre suivant la revendication 13, dans lequel ce mélange comprend du méthyl triéthoxysilane et du  $\gamma$ -aminopropylène triéthoxysilane.
15. Procédé ou tête d'enregistrement à jet d'encre suivant l'une quelconque des revendications 1 à 14, dans lequel le fluorosilane hydrolysable a la formule :
- $$\text{R}^2_m\text{SiR}^3_n\text{R}^4_p$$
- dans laquelle m est 1 ou 2, n est au moins 1, p est 0, 1 ou 2, la somme de m + n + p est 4, chaque R<sup>2</sup> est un groupe organique contenant du fluor, chaque R<sup>3</sup> est un groupe hydrolysable et chaque R<sup>4</sup> est un atome ou groupe non hydrolysable autre que R<sup>2</sup>.
16. Procédé ou tête d'enregistrement à jet d'encre suivant la revendication 15, dans lequel m est 1, n est 3 et p est 0.
17. Procédé ou tête d'enregistrement à jet d'encre suivant les revendications 15 ou 16, dans lequel chaque R<sup>3</sup> est un groupe alcoxy.
18. Procédé ou tête d'enregistrement à jet d'encre suivant les revendications 15, 16 ou 17, dans lequel le fluorosilane est choisi parmi le 1H, 1H, 2H, 2H-perfluorooctyl triéthoxysilane et le 1H, 1H, 2H, 2H-perfluorododécyl triéthoxysilane.
19. Procédé ou tête d'enregistrement à jet d'encre suivant l'une quelconque des revendications 1 à 18, dans lequel cette surface comprend une matière plastique choisie parmi un polyimide, un polycarbonate, un polyester et une polyéther-éther-cétone.

